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Spray deposited carbon nanotubes for organic vapor sensors

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ABSTRACT

In this article a study of chemiresistor sensors based on Single and Multi Wall Carbon Nanotube films deposited at low temperature by means of a spray technique is presented. A dispersion of nanotube powder in a non-polar 1,2-Dichloroethane solvent was used as starting solution. Electron Microscopy in Scanning and Transmission mode were used in order to verify the morphological properties of the deposited films. The conductivity of carbon nanotubes (CNTs) was measured in two organic solvent vapors environments: 2-propanol and carbon-tetrachloride. The solvents used are characterized by different polarities. The results show that the electrical resistance of the sensors increases when exposed to solvent vapors. Finally the effect of Teflon-like and Melanin coatings on the sensitivity yield is presented and discussed.

1. Introduction

By definition, a chemical gas sensor is a device capable of altering its physical properties (electrical conductance, capacitance, or mass) upon exposure to a gaseous chemical compound or mixture of chemical compounds. The change in properties can be observed as an electrical signal and then used to detect the species [1]. Since the early 1990s, research interest in nanotechnology has grown rapidly ranging from new high-performance nanomaterials to nanoscale electronics and Micro-Electro-Mechanical Systems (MEMS). The scientific community working in the field of sensors has also benefited from nanotechnology, especially through the development of advanced nanomaterials, including the most widely studied carbon nanotubes (CNTs) [1].

Since 2000, the possibility to use CNTs for chemical gas sensing applications has attracted extensive research effort for some significant properties. Carbon nanotubes show extreme sensitivity toward changes in the local chemical environment that derives from the susceptibility of their electronic structure to interacting molecules, so the conductance of the semiconductive CNTs is proportional to the number of free carriers [2,3]. The ballistic electronic transport along the CNT axis provides excellent transmission of the altered electrical signal to the external contacts. The long-term performance of CNTs based sensors may be stable due to their chemically robust graphitic surface.

CNTs for gas sensing at room temperature are of great interest because most currently available sensors operate at elevated temperatures [1]. Due to extremely high surface-to-volume ratio, efficient gas adsorption occurs on their surface. The one-dimensional quantum wire nature makes its electronic properties very sensitive to the gas molecules adsorption [4]. Conductivity measurement is then a simple and convenient method to register CNTs response to gas adsorption/desorption [5].

Actually, the more used technique for the CNTs deposition is the Chemical Vapor Deposition, which requires high substrate temperatures, limiting the materials that can be coated. Other methods like electrophoresis and suspension filtering have the disadvantages of using large size substrates, and the film shows poor adhesion on them. Finally, screen printing methods is limited by the degradation of emission tips [6].

2. Material and methods

In the present work, purified powder of Single and Multi Wall Carbon Nanotubes (SWCNTs - MWCNTs) (COMETOX), with a purity degree of about 90 wt%, was used as the sensing material. SWCNTs

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were 5–20 μm long with diameters of up to 2 nm, while MWCNTs were 5–15 μm long with diameters of up to 30 nm. The films were obtained using a spray technique starting from solution of the powder in a rate of 0.1 gr of nanotubes for 100 ml of dispersing medium, allowing to easily deposit CNTs on large areas, with a very good adhesion, without emission tips degradation and intermediate layers.

In order to exploit the properties for monodimensional CNTs, the nonpolar solvent 1,2-Dichloroethane (DCE) was chosen for solution preparation, due to the stronger interactions between the solvent molecules and CNTs with respect to interactions between nanotubes themselves. DCE has been also chosen because it is easily vaporized in ambient conditions and it has low surface tension that gives rise to good wettability of CNTs. To remove the water inside the powder, that push the nonpolar CNTs up to form bundles, preliminarily standard drying process was followed. The powder was washed with warm deionized water, 2-propanol, acetone and DCE [6].

Finally, the CNTs dispersion was prepared following the procedure reported with more details in [7]. An airbrush with Argon as driving gas, at a pressure of $2.5*10^4$ Pa, was used to spray the dispersed nanotubes on the substrates. In order to reach better film uniformity and a fast drying of the samples, the substrates were heated at about 120 °C during the deposition. Homemade aluminum masks were used to select the CNT deposition area. Because of the presence of dangerous substances such as DCE and CNTs, the whole deposition system was placed inside a fume hood.

In Fig. 1 the basic structure of the device is reported. It consists of ~100 nm thick interdigitated gold electrodes with 0.2 mm gap between fingers, deposited by thermal evaporation process on alumina (Al_2O_3) substrates. The CNTs film covers the entire area of gold fingers.

After the spray process, some SWCNT and MWCNT sensors were covered by Teflon-like (CFx) and Melanin films, obtaining four different type of devices. 20 nm thick CFx films were deposited by means of the Ion Beam Sputtering (IBS) technique starting from a Teflon target. 50 nm thick Melanin layers were deposited starting from a solution using the spin coating technique. Teflon has been chosen due to its capacity to swell in presence of vapors, a very important property for sensing applications [8]. Melanin has been used because, starting from its properties to change strongly conductivity as a function of the concentration of moisture present within the molecules [9], we expect a similar behavior with other vapors.

As test gas, 2-propanol and carbon tetrachloride (CCl_4) vapors were used, as polar and nonpolar solvents, respectively. The vapors were obtained by bubbling the analytes with 10 or 20 sccm of dry air, obtaining two different concentrations. The test gases were further diluted by means of a second flow meter and were delivered at a constant flow rate of 100 sccm onto the sensing element kept at 25 °C.

Transmission Electron Microscopy (TEM - FEI Tecnai G2 Spirit, 120 kV energy) was used to evaluate the CNTs dispersion degree in the film. Morphology was investigated by means of Scanning Electon Microscopy (SEM - Zeiss-Σigma microscope with inLens detector, 20 μm aperture, 10 kV energy).

In order to perform the electrical response of the sensors, the current-time characteristics were measured during cyclical exposure to the analyte at room temperature by means of an Agilent B1500A semiconductor parameter analyzer.

In this article only the results related to the sensors that have shown response to the analyte presence: Teflon/SWCNT and Melanin/MWCNT are reported.

3. Results and discussions

Adjusting the substrate temperature, the duration of shots and the delay between them in the spray stage, an homogeneous CNT layer can be obtained. The results are confirmed by the SEM image in Fig. 2. The TEM micrograph in the inset of the same figure shows the good separation among the CNTs, as a result of their good dispersion degree in DCE.

The current I as a function of time curves of the sensors in presence of organic solvent vapors was acquired at fixed voltage ($V=2$ V).

Typical response curves for exposure of SWCNTs to CCl_4 and 2-propanol are schematically depicted in Fig. 3. The chemiresistor exposing time to organic solvent vapors was set to 300 s, then the device was exposed to a pure air flux for the same time.

As can be seen, the conductivity decreases when CNTs are exposed to the solvent vapors, that behave as electron donors going to recombine with nanotube holes.

To evaluate gas sensor characteristics and to compare their performance, we introduce the *sensitivity* parameter defined as:

$$S = \left[(R_{gas} - R_{air})/R_{air}\right] \times 100 \quad (1)$$

where R is the electrical resistance measured between the electrodes.

The sensitivity trend recorded for the SWCNTs samples subjected to cyclic flow of 2-propanol (0,1%–0,5% volume fraction in air) and CCl_4 (0,8%–1,6% volume fraction in air) is shown in Fig. 4. The experimental data show a good reversibility of the adsorption-desorption process. The positive trend of the electrical signals can

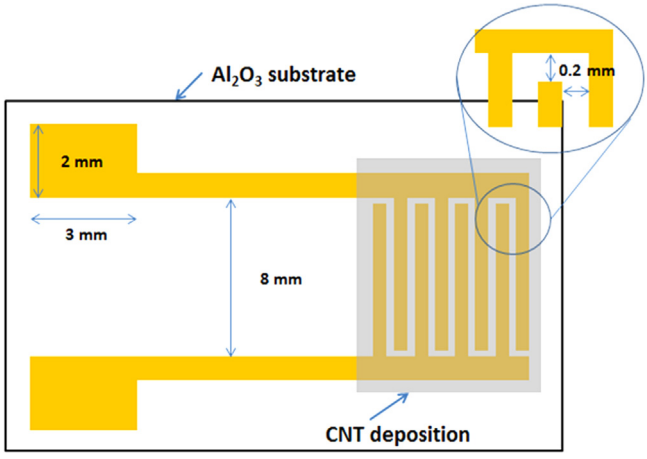

Fig. 1. Device layout with the sprayed carbon nanotube film.

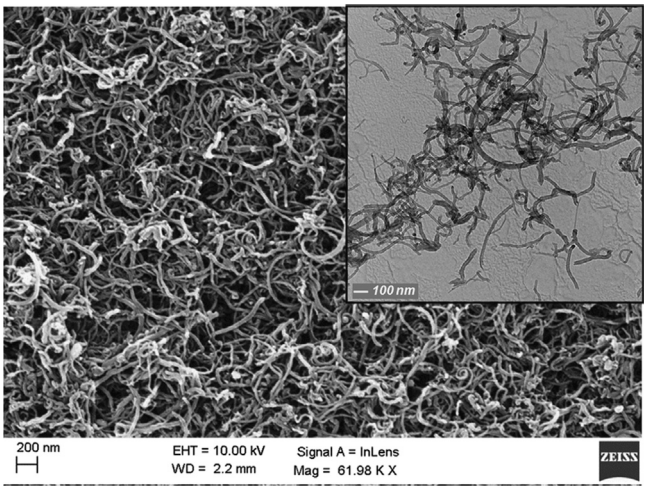

Fig. 2. SEM image of a SWCNTs film on a silicon substrate. In the inset the TEM micrograph of four shots of the dispersion is shown, with a white scale bar of 100 nm.